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(51) International Patent Classification: A41D 19/015, B32B 25/14, B32B 25/16, C08L 33/02, C08L 33/20	A1	(11) International Publication Number: WO 00/47070 (43) International Publication Date: 17 August 2000 (17.08.2000)
(21) International Application Number: PCT/US00/03135 (22) International Filing Date: 07 February 2000 (07.02.2000) (30) Priority Data: 09/248,938 12 February 1999 (12.02.1999) US 09/410,282 30 September 1999 (30.09.1999) US (60) Parent Application or Grant ALLEGIANCE CORPORATION [/]; (). YEH, Yun-Siung, Tony [/]; (). ZHU, Duanna [/]; (). WONG, Wei, Cheong [/]; (). TAN, Sharon, Mi, Lyn [/]; (). SCHAAFSMA, Paul, E. ; ().		Published
(54) Title: POWDER-FREE NITRILE-COATED GLOVES WITH AN INTERMEDIATE RUBBER-NITRILE LAYER BETWEEN THE GLOVE AND THE COATING (54) Titre: GANTS RECOUVERTS D'UN REVETEMENT EN NITRILE EXEMPT DE POUDRE EQUIPES D'UNE COUCHE INTERMEDIAIRE EN CAOUTCHOUC NITRILE PLACEE ENTRE LE GANT ET LE REVETEMENT		
(57) Abstract <p>Powder-free natural rubber and synthetic elastomeric articles, in particular, gloves, having an inner coating of a nitrile rubber with an intermediate layer of a rubber blend comprised of natural or synthetic rubber and nitrile rubber interposed between the nitrile coating and the base glove and their method of manufacture are described. The intermediate layer of the rubber blend interposed between the coating and the glove imparts a unique surface texture to the glove which aids donning and eliminates self-sticking of the inner glove surfaces, especially after the glove has been sterilized by radiation. Additionally the gloves of the invention exhibit good grippability, good donnability, superior tensile strength, elongation to break and stress at 500 % elongation.</p> (57) Abrégé <p>L'invention concerne, d'une part, des articles en caoutchouc naturel exempts de poudre et en élastomères de synthèse, en particulier des gants, recouverts d'un revêtement intérieur en caoutchouc nitrile et équipés d'une couche intermédiaire faite d'un mélange de caoutchouc à base de caoutchouc naturel ou synthétique et de caoutchouc nitrile placée entre le revêtement en nitrile et le gant d'origine et, d'autre part, de la technique de fabrication connexe. La couche intermédiaire faite d'un mélange de caoutchouc, placée entre le revêtement et le gant, confère à ce dernier une texture superficielle unique qui favorise son enfillement et élimine l'auto-adhérence de sa surface intérieure, notamment après stérilisation par irradiation. En outre, les gants selon l'invention présentent une bonne adhérence, une facilité d'enfillement, ainsi qu'une résistance à la traction et un allongement à la rupture supérieurs et une contrainte à un allongement de 500 % inférieure.</p>		

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(21) International Application Number: PCT/US00/03135 (22) International Filing Date: 7 February 2000 (07.02.00) (30) Priority Data: <table border="0"><tr><td>09/248,938</td><td>12 February 1999 (12.02.99)</td><td>US</td></tr><tr><td>09/410,282</td><td>30 September 1999 (30.09.99)</td><td>US</td></tr></table> (71) Applicant: ALLEGIANCE CORPORATION [US/US]; Building KB, 1430 Waukegan Road, McGaw Park, IL 60085-6787 (US). (72) Inventors: YEH, Yun-Siung, Tony; 1313 Amy Lane, Libertyville, IL 60048 (US). ZHU, Duanna; 250 S. Rt. 59 #101, Ingelside, IL 60041 (US). WONG, Wei, Cheong; 111 Jalan Bahagia, Taman Mewah, 09600, Lunas, Kedah (MY). TAN, Sharon, Mi, Lyn; 8 Jalan Halia, Georgetown, Penang 10470 (MY). (74) Agent: SCHAAFSMA, Paul, E.; Allegiance Corporation, 1430 Waukegan Road, McGaw Park, IL 60085-6787 (US).		09/248,938	12 February 1999 (12.02.99)	US	09/410,282	30 September 1999 (30.09.99)	US	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
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Description

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2 "POWDER-FREE NITRILE-COATED GLOVES WITH
3 AN INTERMEDIATE RUBBER-NITRILE LAYER BETWEEN THE GLOVE AND THE COATING"
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6 **BACKGROUND OF THE INVENTION**

7 The majority of commercially available powder-free latex gloves are
8 manufactured by first preparing a powdered glove on-line and then removing the
9 powder from the glove by chlorination and rinsing off-line. The chlorination
10 process oxidizes the natural rubber surface of the glove thereby providing
11 improved dry donning characteristics. Chlorination also removes any powder
12 deposited on the gloves during the rinsing operation.

13 Other powder free gloves have been produced by using powder free
14 coating technology in combination with chlorination or other post treatment
15 processes. Some of these coated gloves use a manufacturing process which
16 requires that the rubber substrate be treated with acid or other harsh chemicals
17 to improve adhesion of the coating to the base rubber glove. This additional
18 chemical processing step is not preferable in glove manufacturing because the
19 chemicals used are generally corrosive and/or difficult to handle in large scale
20 production processes. Additionally, most of the coated and non-coated gloves
21 do not have acceptable donning characteristics with respect to damp and wet
22 skin, which is one of the critical product requirements for surgical glove
23 applications. Finally, some of these gloves also exhibit self-sticking between the
24 inner glove surfaces which create difficulties for health care workers trying to don
25 the gloves in a sterile environment.

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SUMMARY OF THE INVENTION

The present invention provides a powder-free, inner-nitrile rubber coated, natural rubber or synthetic elastomer glove for medical and industrial applications which has good donning characteristics and good grippability (as measured by the coefficient of friction of the donning and gripping surfaces). The glove of the invention also exhibits good tensile strength, stress at 500% elongation and elongation to break.

The inner coating on the gloves of the invention is a cross-linked nitrile rubber blended with a lubricant. Interposed between the nitrile rubber coating and the base elastomeric glove is an intermediate layer of a rubber blend comprised of natural or synthetic rubber and nitrile rubber. Comparative testing demonstrates that the inventive gloves have improved adhesion between the coating and the base glove as compared to those coated gloves which do not contain the intermediate layer of rubber blend. The gloves of the invention do not show any appearance of surface sticking between the inner surfaces and/or the outer surfaces and also exhibit good donning with respect to both dry and wet skin. The inventive gloves also have a unique surface texture which improves donnability.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1A is a scanning electron microscope (SEM) photograph (x2000 magnification) of the interior surface of a prior art natural rubber latex glove

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1 which contains neither an intermediate layer nor an inner nitrile coating. The
2 glove has been chlorinated and lubricated.
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3 Figure 1B is a scanning electron microscope (SEM) photograph (x2000
4 magnification) of the interior surface of a natural rubber latex glove in
15 5 accordance with the invention which has an intermediate layer containing 2.5%
6 total solids and an inner nitrile coating containing 5.0% total solids. The glove
7 has been chlorinated and lubricated.
20

8 Figure 2A is a scanning electron microscope (SEM) photograph (x2000
9 magnification) of the interior surface of a natural rubber latex glove which does
25 10 not contain an intermediate layer but which has a nitrile coating. The glove has
11 not been chlorinated or lubricated.

12 Figure 2B is a scanning electron microscope (SEM) photograph (x2000
13 magnification) of the interior surface of a natural rubber latex glove which has an
14 intermediate layer but which has no nitrile coating. The glove has not been
35 15 chlorinated or lubricated.

16 PREFERRED EMBODIMENTS OF THE INVENTION

17 The gloves of the invention are comprised of a natural rubber, nitrile,
18 polychloroprene, polybutadiene, polyvinylchloride, polyurethane, synthetic
45 19 polyisoprene, styrene diblock and triblock copolymers, or other synthetic
20 elastomers, including blends thereof, which have on their inner surface a coating
21 comprised of a cross-linked nitrile rubber blended with lubricant with an
50 22 intermediate layer of a rubber blend of natural or synthetic rubber and nitrile

1 rubber interposed between the elastomeric glove and the coating of nitrile
2 rubber.

3 The natural rubber latex used to form the base glove may be compounded
4 with stabilizers, a crosslinker, a vulcanization activator, a vulcanization
5 accelerator, an antioxidant, an antiozonant and optionally, white or other colored
6 pigments.

7 Suitable stabilizers include oleates, stearates, alginates, polyacrylates,
8 xanthan gums, caseinates or other nonionic and ionic surfactants. Typical
9 crosslinkers which may be used in the compounding formulation include sulfur or
10 other organic peroxides. Suitable vulcanization activators include metal oxides,
11 such as magnesium oxide, lead oxide, and preferably, zinc oxide. The
12 vulcanization accelerator may be chosen from mercaptobenzothiazoles and their
13 derivatives, dithiocarbamates and their derivatives, sulfur donors, guanidines and
14 aldehyde-amine reaction products. Suitable antioxidants include hindered
15 arylamines or polymeric hindered phenols. Typical antiozonants which may be
16 used in the compounding formulation include paraffinic waxes, microcrystalline
17 waxes and intermediate types of waxes (which are blends of both paraffinic and
18 microcrystalline waxes). Typical white pigments that may be used include
19 titanium dioxide and zinc oxide.

20 Synthetic diene based elastomers used to form the base glove such as
21 polybutadiene, synthetic polyisoprene, nitrile, polychloroprene and its blends can
22 be compounded with similar compounding ingredients as set forth above. Other

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1 synthetic thermoplastic elastomeric materials used for the base glove such as
2 polyvinylchloride, polyurethanes, styrene diblock and triblock copolymers and its
3 blends do not require crosslinking to prepare a glove with the desired physical
4 properties. Accordingly, these synthetic elastomers may be compounded with
5 stabilizers, antioxidants, antiozonants and color pigments as described above.

6 Those skilled in the art will readily be able to vary the total solid content of
7 the dipping formulation to form the base glove with the desired thickness and the
8 compounding ingredients in the dipping formulation to suit the particular
9 elastomers used to form the base glove as well as the final article desired.

10 An intermediate layer of a rubber blend comprised of a natural or synthetic
11 rubber and nitrile rubber is interposed between the elastomeric glove and the
12 nitrile coating by dipping the glove a second time after coagulation has formed
13 the base glove or first elastomeric layer. The nitrile rubber latex used to form the
14 intermediate rubber blend is a carboxylated acrylonitrile butadiene terpolymer
15 dispersion. The carboxylated acrylonitrile butadiene terpolymer preferably has
16 an acrylonitrile content of about 25 to about 40 parts, a butadiene content of
17 about 55 to about 68 parts and a carboxylic acid content of about 3 to about 6
18 parts. The carboxylated acrylonitrile butadiene terpolymer most preferably has
19 an acrylonitrile/butadiene/carboxylic acid ratio of 39/58/3.

20 Alternatively, the nitrile rubber latex used to form the intermediate rubber
21 blend is an acrylonitrile butadiene based copolymer dispersion or a dispersion of
22 a hydrogenated acrylonitrile butadiene copolymer. If the latter polymer is used,

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1 the degree of hydrogenation is preferably greater than about 85%. Preferably,
2 the acrylonitrile content of these copolymers varies from about 25 to about 50
3 parts and the butadiene content varies from about 50 to about 75 parts. Most
4 preferably, the acrylonitrile content of these copolymers varies from about 25 to
5 about 45 parts and the butadiene content varies from about 50 to about 75 parts.

6 For a base glove or first elastomeric layer comprised of natural rubber, the
7 intermediate layer is preferably comprised of a blend of natural rubber and nitrile
8 rubber. Preferably, the blend ratio is about 5 parts natural rubber/95 parts nitrile
9 rubber (a blend ratio of 5/95) to about 95 parts natural rubber/5 parts nitrile
10 rubber (a blend ratio of 95/5). Most preferably, the blend ratio is about 40/60 to
11 about 90/10. For a base glove comprised of a synthetic rubber, the intermediate
12 layer is preferably comprised of a blend of the same synthetic rubber used to
13 form the base glove and nitrile rubber. Preferably, the blend ratio is about 5 parts
14 synthetic rubber/95 parts nitrile rubber (a blend ratio of 5/95) to about 95 parts
15 synthetic rubber/5 parts nitrile rubber (a blend ratio of 95/5). Most preferably, the
16 blend ratio is about 40/60 to about 90/10. The rubber blend latex which forms
17 the intermediate layer is compounded with stabilizers, a crosslinker, a
18 vulcanization activator, a vulcanization accelerator and the following optional
19 ingredients: an antioxidant, an antiozonant and white or colored pigments.

20 Suitable stabilizers include oleates, stearates, alginates, polyacrylates,
21 xanthan gums, caseinates and other nonionic and ionic surfactants. Preferably

1 the stabilizers are caseinates and surfactants. Most preferably, the stabilizer is a
2 non-ionic and/or ionic surfactant.

3 Typical crosslinkers used in the compounding formulation include sulfur,
4 and organic peroxides. Preferably, the crosslinker is sulfur.

5 Suitable vulcanization activators include metal oxides, such as
6 magnesium oxide, lead oxide and preferably, zinc oxide. The vulcanization
7 accelerator may be chosen from mercaptobenzothiazoles and their derivatives,
8 dithiocarbamates and their derivatives, sulfur donors, guanidines and aldehyde-
9 amine reaction products.

10 Suitable antioxidants include hindered arylamines and polymeric hindered
11 phenols. Typical antiozonants which may be used in the compounding
12 formulation include paraffinic waxes, microcrystalline waxes and intermediate
13 types of waxes (which are blends of both paraffinic and microcrystalline waxes).
14 Typical white pigments that may be used include titanium dioxide and zinc oxide.

15 The compounding ingredients used to prepare the intermediate rubber
16 blend layer dispersion and their relative proportions are set forth below in Table
17 1. The total percent solid of this dispersion is adjusted to be less than about
18 45%. During the dipping of the intermediate rubber blend latex, chemical
19 contaminants such as ionic species, especially bivalent ions from the coagulated
20 natural rubber layer or synthetic rubber layer may inadvertently be introduced
21 into the rubber blend latex. Because of the increasing concentration of these
22 contaminants, the rubber blend latex should be adequately stabilized to prevent

1 latex flocculation. It is important that the rubber blend latex be stabilized
2 adequately toward ionic species and yet not be too stable to prevent the
3 coagulation of the rubber blend latex onto the rubber layer that forms the base
4 glove or first elastomeric layer. If the percent solid content of the rubber blend
5 latex is low, the rubber blend latex is not as stable as a high percent solid
6 content rubber blend latex and thus additional stabilizers are typically added
7 during the compounding of the rubber blend latex. The total amount of natural
8 rubber or synthetic rubber and nitrile rubber will be about 100 parts.

Table 1

Dispersion Ingredient	Dry or Active Parts By Weight
Natural rubber or Synthetic rubber dispersion	About 0 to about 100
Nitrile rubber dispersion	About 100 to about 0
Stabilizers	About 0.01 to about 10
Crosslinker	About 0.1 to about 20
Vulcanization Accelerator	About 0.1 to about 20
Vulcanization Activator	About 0.1 to about 20
Antioxidants (optional)	About 0.1 to about 10
Antiozonant (optional)	About 0.1 to about 10
White or colored pigment (optional)	About 0.1 to about 10

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11 The nitrile rubber latex used to coat the interior surface of the formed
12 glove, i.e., disposed on the intermediate layer, is a carboxylated acrylonitrile

1 butadiene rubber dispersion, preferably, a dispersion of a carboxylated
2 acrylonitrile butadiene terpolymer containing an acrylonitrile content of about 25
3 to about 40 parts, a butadiene content of about 55 to about 68 parts and a
4 carboxylic acid content of about 3 to about 6 parts. More preferably, the nitrile
5 rubber latex is a blend of two carboxylated acrylonitrile butadiene rubber
6 dispersions of different acrylonitrile/butadiene/carboxylic acid ratios [A and B in
7 Table 2]. Most preferably, the nitrile rubber latex is a dispersion blend of a
8 carboxylated acrylonitrile butadiene rubber with an
9 acrylonitrile/butadiene/carboxylic acid ratio of about 39/58/3 and a carboxylated
10 acrylonitrile butadiene rubber with an acrylonitrile/butadiene/carboxylic acid ratio
11 of about 39/55/6. The blend ratio of the two carboxylated acrylonitrile butadiene
12 terpolymers is about 1/99 to about 99/1. Preferably, the blend ratio is about
13 75/25 to about 25/75. Most preferably, the blend ratio is about 50/50. A single
14 nitrile rubber dispersion may be used instead of a nitrile blend dispersion for
15 ease of material handling and manufacturing, preferably a carboxylated
16 acrylonitrile butadiene rubber with an acrylonitrile/butadiene/carboxylic acid ratio
17 of about 39/55/6. For use as part of the coating on the interior of the gloves of
18 the invention, the nitrile rubber dispersion is additionally compounded with a
19 crosslinker, vulcanization accelerator, vulcanization activator, lubricant, and
20 optionally, a biocide.

21 Alternatively, the nitrile rubber latex used to coat the interior surface of the
22 formed glove, i.e. disposed on the intermediate layer, is an acrylonitrile
23 butadiene based copolymer dispersion or a hydrogenated acrylonitrile butadiene

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1 copolymer. If the latter polymer is used, the degree of hydrogenation is
2 preferably greater than about 85%. Preferably, the acrylonitrile content of these
3 copolymers varies from about 25 to about 50 parts and the butadiene content
4 varies from about 50 to about 75 parts. Most preferably, the acrylonitrile content
5 of these copolymers varies from about 25 to about 45 parts and the butadiene
6 content varies from about 50 to about 75 parts. The nitrile rubber latex is
7 preferably a blend of two acrylonitrile butadiene rubber dispersions of different
8 acrylonitrile/butadiene ratios. [A and B in Table 2]

9 The crosslinker may be chosen from sulfur, organic peroxides and metal
10 oxides. Preferably, the crosslinker is selected from the group consisting of sulfur
11 and metal oxides. Most preferably, the crosslinker is sulfur.

12 The vulcanization activator may be metal oxides. The preferred metal
13 oxides are magnesium and zinc oxide. The most preferred metal oxide is zinc
14 oxide.

15 The vulcanization accelerator is chosen from mercaptobenzothiazoles and
16 their derivatives, dithiocarbamates and their derivatives, sulfur donors,
17 guanidines and aldehyde-amine reaction products. Preferably, the accelerator
18 chosen from the dithiocarbamates and their derivatives. Most preferably, the
19 accelerator is a dispersion of zinc dibutyldithiocarbamate.

20 The lubricant may be chosen from organic powders, inorganic powders,
21 silicones, stearates, fluorochemicals, petroleum oils, organic esters, polyglycols,
22 synthetic hydrocarbons and phosphates. Preferably, the lubricant is a siloxane

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1 based silicone emulsion. Most preferably, the silicone is a poly(alkylsubstituted
2 siloxane) emulsion.

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3 Optionally, a small amount of biocide may be added into the nitrile rubber
4 latex to inhibit the growth of microorganisms. The biocide may be chosen from
15 5 the following classes of individual biocides but is not limited to them: phenolics,
6 halogen compounds, quaternary ammonium compounds, metal-containing
20 7 compounds, anilides, amines, alkanolamines, nitro compounds, organosulfur and
8 sulfur-nitrogen compounds. Preferably, the biocide is chosen from the industrial
9 biocides generally used in paints, latexes, polymer emulsions and water based
25 10 coating systems. Most preferably, the biocide is chosen from the biocide list
11 approved by the FDA for food and food-packaging applications and is compatible
12 with the nitrile rubber latex. Materials approved by the FDA are listed in the
30 13 *Federal Register* under appropriate sections based on specific applications.
14 They can be seen in the reference: "Biocides", Encyclopedia of Polymer Science
35 15 and Engineering, Second Edition, Volume 2, John Wiley & Sons, 1985, pages
16 202 – 219 which is hereby incorporated by reference. Examples of suitable
40 17 biocides are formaldehyde based and triazine based biocides.

18 The compounding ingredients used to prepare the nitrile rubber powder
19 free dispersion and their relative proportions are set forth below in Table 2. The
45 20 total amount of [A] and [B] will be about 100 parts.

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TABLE 2

DISPERSION INGREDIENT	DRY OR ACTIVE PARTS BY WEIGHT
Nitrile rubber dispersion [A]	About 0 to about 100
Nitrile rubber dispersion [B]	About 100 to about 0
Crosslinker	About 0.1 to about 20
Vulcanization Accelerator	About 0.1 to about 20
Vulcanization Activator	About 0.1 to about 20
Lubricant	About 0.1 to about 25
Biocide (optional)	About 0.1 to about 5

Alternatively, the powder free dispersion used to coat the interior surface of the formed glove, i.e. disposed on the intermediate layer, is a dispersion blend of nitrile rubber and other synthetic rubber. Preferably, the blend ratio of the nitrile rubber and synthetic rubber is about 50/50 to about 99/1. Most preferably, the blend ratio of the nitrile rubber and synthetic rubber is about 75/25 to about 95/5. Synthetic rubber dispersions may be chosen from the following classes of synthetic materials but is not limited to them: polyurethanes, acrylics, synthetic polyisoprene, polybutadiene and other synthetic diene based elastomers. The compounding ingredients used to prepare the synthetic blend powder free dispersion and their relative proportions are set forth below in Table 3. The total amount of [A] and [B] will be about 100 parts.

TABLE 3

DISPERSION INGREDIENT	DRY OR ACTIVE PARTS BY WEIGHT
Nitrile rubber dispersion [A]	About 0 to about 100
Synthetic rubber dispersion [B]	About 100 to about 0
Crosslinker	About 0.1 to about 20
Vulcanization Accelerator	About 0.1 to about 20
Vulcanization Activator	About 0.1 to about 20
Lubricant	About 0.1 to about 25
Biocide (optional)	About 0.1 to about 5

Those skilled in the art will readily be able to vary the compounding ingredients in the dipping formulation to suit the final synthetic or natural rubber article desired. For example, if a carboxylated acrylonitrile butadiene terpolymer dispersion is used, the crosslinker and the vulcanization accelerator may not be needed in the dipping formulation since the metal oxide vulcanization activator may also function as a crosslinker to crosslink the nitrile rubber via ionic bonding.

Alternatively, the lubricant may be added separately to the dispersion during the manufacturing of the nitrile dispersion or the nitrile may be chemically modified to incorporate lubrication characteristics during polymerization. An example of the chemical modification approach is to incorporate a silicone based compound into the nitrile by chemical grafting or by polymerization. In these

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1 cases, the addition of the lubricant in the dipping formulation as listed in Table 2
2 and Table 3 may not be necessary.

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3 The nitrile-based powder-free dispersion can be used to coat the interior
4 of a variety of natural rubber and synthetic elastomer articles, including surgical
5 and examination gloves, industrial gloves, finger cots, tubing, ultrasound probe
6 covers, protective sheaths and catheter balloons for medical and industrial
7 applications.

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8 The gloves fabricated in accordance with the present invention may be
9 prepared as follows. A mold in a contoured shape of a glove is first oven dried
10 and then dipped into an alcohol or water-based coagulant dispersion comprising
11 calcium nitrate, powder (calcium carbonate or cornstarch), wetting agent and
12 water or alcohol (for alcohol based coagulant dispersion). The coagulant layer
13 deposited on the glove former is then dried. The glove former is then dipped into
14 the compounded natural rubber latex or synthetic elastomer dispersion and a film
15 of the natural rubber or synthetic elastomer is coagulated on the glove former.
16 While still on the former, the layer of coagulated natural rubber or synthetic
17 elastomer is then dipped into a blend of natural rubber and nitrile rubber
18 dispersion or a blend of synthetic rubber and nitrile rubber dispersion to form an
19 intermediate layer on the glove. The glove is optionally leached with water and
20 then dipped into a powder-free dispersion comprising a nitrile rubber (or a
21 dispersion blend of nitrile rubber and other synthetic rubbers), a lubricant, a
22 cross-linker, a vulcanization accelerator and a vulcanization activator as set forth

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1 in Table 2. The former carrying the nitrile rubber coated natural rubber or
2 synthetic elastomer glove with an intermediate layer of natural rubber and nitrile
3 rubber or synthetic rubber and nitrile rubber interposed between the nitrile rubber
4 coating and the base glove is then cured in an oven. The former is removed
5 from the oven and the glove is then stripped from the former.

6 To prepare the powder free coated gloves, the gloves are post-processed
7 by chlorination as follows. The coated gloves are initially turned inside out with
8 the coated surfaces on the outside of the gloves. The gloves are optionally pre-
9 rinsed with water two times (for about 2.5 minutes per time) and immersed in an
10 aqueous chlorinated solution in a chlorinator for about at least 6 minutes. The
11 chlorine concentration may vary from about 50 ppm to about 1500 ppm.
12 Preferably the chlorine concentration is about 150 to about 700 ppm. Most
13 preferably, the chlorine concentration is about 250 ppm to about 350 ppm. After
14 chlorination, the chlorinated solution is neutralized by adding a base (e.g.,
15 sodium hydroxide or ammonium hydroxide) to the solution and the gloves are
16 then tumbled for about 4 minutes or until the pH of the solution is about 7 or
17 above. The neutralized solution is then drained and the gloves are rinsed with
18 water for about 2.5 minutes. The gloves may be rinsed three more times (for
19 about 2.5 minutes per time) to remove traces of the chlorinated solution.

20 For medical examination and industrial glove applications, after rinsing,
21 the gloves are dried at about 55°C for about 20 minutes. The gloves are then

1 turned again so that the coated surface is on the inside of the glove. The gloves
2 are then dried again at about 50°C for about 5 minutes.

3 Alternatively, for medical examination and industrial applications, the
4 powder-free coated gloves of the invention are prepared as set forth above
5 except the chlorination processing steps are modified as follows. After stripping
6 from the former, the coated gloves are optionally pre-rinsed with water and
7 immersed in an aqueous chlorinated solution in a chlorinator for at least about 6
8 minutes. The chlorine concentration may vary from about 50 ppm to about 1500
9 ppm. Preferably, the chlorine concentration is about 150 to about 700 ppm.
10 Most preferably, the chlorine concentration is about 250 ppm to about 350 ppm.
11 After chlorination, the chlorinated solution is neutralized by adding a base to the
12 solution and the gloves are then tumbled for about 4 minutes or until the pH of
13 the solution is about 7 or above. The neutralized solution is then drained and the
14 gloves are rinsed with water for about 2.5 minutes. The gloves are then rinsed
15 three more times to remove traces of the chlorinated solution. After rinsing, the
16 gloves are dried at about 55°C for at least 20 minutes or until the gloves are
17 dried. The powder-free coated gloves are now ready for packing. Preferably,
18 the above described post-processing steps are suitable for processing a coated
19 glove with a bead on the cuff. The beading step can be applied before or after
20 dipping of the former with the intermediate rubber blend layer into the powder-
21 free nitrile rubber dispersion as described above.

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1 For surgical glove applications, the gloves are preferably lubricated after
2 chlorination with a lubricant solution to provide good donning characteristics with
3 respect to damp and wet skin. For these applications the rinsed gloves are
4 removed from the chlorinator and placed in an extractor/lubricator/dryer. The
5 gloves are extracted to remove excess water and a lubricant solution is then
6 applied to the coating surface, e.g., by spraying or by tumbling. The lubrication
7 solution is preferably comprised of about 0.1 wt % to about 2 wt. %
8 cetylpyridinium chloride and about 0.01 wt % to about 2 wt. % silicone emulsion.
9 After the lubricant application, the gloves are dried at about 55° C for about 20
10 minutes. After the first dry, the gloves are turned inside out so that the coated
11 surfaces are on the inside of the glove. The gloves are then dried again at about
12 50 ° C for about 5 minutes.

13 Other suitable lubricants that may be used to provide wet and damp
14 donning characteristics are nonionic and ionic surfactants. Among these
15 surfactants, the cationic and amphoteric surfactants are most preferred for these
16 applications. These surfactants may also be combined with other lubricants
17 such as silicones, stearates, or other water soluble polymers such as chitosan,
18 polyethylene oxide or polyvinyl alcohol, to provide acceptable donning features
19 for surgical glove applications

20 The finished gloves are packaged and sent for sterilization by gamma or
21 electron beam radiation.

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1 The gloves of the invention have a thickness of at least about 0.003
2 inches. Preferably, the thickness of the gloves ranges between about 0.004
3 inches and about 0.020 inches. Most preferably, the glove thickness is between
4 about 0.005 and about 0.0018 inches.

5 The gloves of the invention exhibit a tensile strength of greater than about
6 1300 psi, preferably greater than about 2600 psi and most preferably, greater
7 than about 3500 psi. The stress at 500% of the gloves of the invention is less
8 than about 3000 psi, preferably less than about 2000 psi and most preferably,
9 less than about 1000 psi. The gloves of the invention have an elongation at
10 break greater than about 200 %, preferably greater than about 500 % and most
11 preferably greater than about 800%.

12 The gloves of the invention exhibit a dry kinetic COF of less than about
13 0.6 for the donning (coated) inner surface and greater than about 0.6 for the
14 gripping (uncoated) outer surface. Preferably, the dry kinetic COF is less than
15 about 0.5 for the donning surface and greater than about 0.7 for the gripping
16 surface. Most preferably, the dry kinetic COF is less than about 0.4 for the
17 donning surface and greater than about 0.8 for the gripping surface.

18 The glove thickness is measured by a digital thickness gauge and is the
19 average of three measurements in the palm area. Tensile strength, stress at
20 500% elongation and elongation to break are measured according to ASTM
21 D412-92. Dry kinetic COF is measured according to ASTM D1894.

1 The gloves of the invention after gamma and electron beam sterilization at
2 a dose range of about 25 kGy to about 80 kGy show no appearance of surface
3 sticking between the inner surfaces and/or outer surfaces. The gloves of the
4 invention were further characterized by scanning electron microscopy (SEM) at
5 x2000 magnification which illustrated the difference in surface morphology
6 between gloves with and without an intermediate layer and the nitrile inner
7 coating.

8 Figure 1A is a SEM photograph of the inner glove surface of a prior art
9 powder free natural rubber latex glove without the intermediate rubber blend
10 layer and the inner nitrile coating layer and Figure 1B is a SEM photograph of
11 the inner glove surface of the inventive powder free coated natural rubber latex
12 glove. Comparison of the two figures clearly shows that the coated glove
13 surface exhibits rough domains on the order of about 10 micrometers with
14 unique surface texturing, whereas the non-coated natural rubber surface shows
15 a typical natural rubber surface with microdomains of less than 1 micrometer.
16 The unique surface texture of the gloves of the invention provides a reduced
17 surface contact area which contributes to the reduction or elimination of self-
18 sticking of the inner glove surfaces. The unique surface texture also facilitates
19 glove donning.

20 Figures 2A and 2B illustrate that the unique surface texturing on the
21 coated glove is mainly due to the presence of the intermediate rubber blend
22 layer. Figure 2A is a SEM photograph of the inner glove surface of a nitrile

1 coated natural rubber latex glove without the intermediate rubber blend layer and
2 Figure 2B is a SEM photograph of the inner glove surface of a natural rubber
3 latex glove coated with just the intermediate rubber blend layer. It is apparent
4 that the intermediate rubber blend coated surface shown in Figure 2B exhibits
5 numerous cavities with pore diameters of about 5 - 10 micrometers which are
6 absent in the nitrile coated surface without the intermediate rubber blend layer.

7 The improved adhesion exhibited by the gloves with an intermediate layer
8 or rubber blend as compared to similarly coated gloves which do not contain the
9 intermediate layer of rubber blend is illustrated by the following comparative
10 example.

11 COMPARATIVE EXAMPLE 1.

12 A nitrile-coated natural rubber latex glove with an intermediate natural
13 rubber-nitrile layer between the glove and the nitrile coating was prepared as
14 follows. A glove former was pre-heated in an oven at about 50°C for about 2
15 minutes. The preheated former then was dipped into a stirred, water based
16 coagulant suspension maintained at a temperature between about 50°C to about
17 55°C. The coagulant-dipped former was then returned to the heated oven for
18 about 2 to about 3 minutes to dry the coagulant layer.

19 The coagulant-coated former was dipped into compounded natural rubber
20 latex for a time sufficient to produce the desired glove thickness. The natural
21 rubber latex was compounded with stabilizers, crosslinker, vulcanization
22 activator, vulcanization accelerators, antioxidant, antiozonant and white pigment.

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1 The solid content of the compounded latex was about 40 wt %. The former
2 bearing the coagulated latex was then removed from the compounded natural
3 rubber latex and immediately dipped into a second rubber blend latex for about
4 13 to 15 seconds. The rubber blend latex comprised about 0.75% compounded
5 natural rubber latex and about 0.75% of carboxylated acrylonitrile butadiene
6 latex and about 98.5% water. The formulation of the compounded natural rubber
7 latex used in this rubber blend latex was the same as the one used in the first
8 latex dipping. The acrylonitrile/butadiene/carboxylic acid ratio of the nitrile rubber
9 was 39/58/3.

10 The former was removed from the second rubber blend latex and leached
11 in water maintained at about 50°C for about 5 minutes. The former was then
12 dipped into a compounded nitrile blend latex with a total solid content of about
13 5% to form a coating on the intermediate natural rubber-nitrile blend layer. The
14 nitrile blend was comprised of a 50/50 blend of two carboxylated acrylonitrile
15 butadiene rubber latices with two different acrylonitrile/butadiene/carboxylic acid
16 ratios, 39/58/3 and 39/55/6. The nitrile blend latex was further compounded with
17 1 part of sulfur dispersion (crosslinker), 1 part of ZDBC dispersion (vulcanization
18 accelerator), 3 parts of ZnO dispersion (vulcanization activator) and 15 parts of
19 silicone emulsion. The former was removed from the compounded nitrile blend
20 latex and placed in an oven at about 125°C for about 20 minutes to cure the
21 glove. The former bearing the glove was then removed from the oven and
22 allowed to cool. The glove was then stripped from the former.

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1 The adhesion of the nitrile coating was evaluated qualitatively using two
2 samples of each glove. In this test, the coated glove surface in the palm and
3 finger areas was stretched to about 500% and the coating was rubbed
4 repeatedly using the thumb. The coated surface was then visually examined for
5 coating flakes and powdery substance. The adhesion of the coating was rated
6 qualitatively on a scale of 1 to 5, 1 being the worst with the entire coating flaking
7 off the rubber substrate and 5 being the best with no visual appearance of
8 powdery substance on the surface of the glove. Using this test, the adhesion of
9 the inventive coating was excellent with a rating of 5 on a scale of 1 to 5, i.e., no
10 flaking or shedding of the powder was observed after stretching the glove to
11 about 500% and rubbing it repeatedly with the thumb.

12 COMPARATIVE EXAMPLE 2.

13 A nitrile-coated natural rubber latex glove without an intermediate natural
14 rubber-nitrile layer between the glove and the nitrile coating was prepared as
15 follows. A glove former was pre-heated in an oven at about 50°C for about 2
16 minutes. The preheated former was dipped into a stirred, water based coagulant
17 suspension maintained at a temperature between about 50°C to about 55°C.
18 The coagulant-dipped former was then returned to the heated oven for about 2
19 to about 3 minutes to dry the coagulant layer.

20 The coagulant-coated former was dipped into a compounded natural
21 rubber latex for a time sufficient to produce the desired glove thickness. The
22 natural rubber latex was compounded with stabilizers, crosslinker, vulcanization

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1 activator, vulcanization accelerators, antioxidant, antiozonant and white pigment.
2 The solid content of the compounded latex was about 40 wt %. The former
3 bearing the coagulated latex was then removed from the compounded natural
4 rubber latex and leached in water maintained at about 50°C for about 5 minutes.
5 The former was then dipped into a compounded nitrile blend latex with a total
6 solid content of about 5% to form a coating on the intermediate natural rubber-
7 nitrile blend layer. The nitrile blend coating formulation was the same as
8 described in comparative example 1.

9 The adhesion of the nitrile coating was fair with a rating of 3 on a scale of
10 1 to 5, i.e., powdery material was shed from the glove after it was stretched to
11 about 500% and rubbed repeatedly with a thumb.

12 The invention is further illustrated by the following examples. It is
13 understood that one of ordinary skill in the art will understand how to vary the
14 times and temperatures of the process in accordance with the article
15 manufactured, the specific elastomer or blend employed, the particular
16 formulation ingredients selected and the percent solid content of the rubber and
17 rubber blend latex. Similarly, one of ordinary skill in the art will know how to
18 select a post-processing method compatible with his individual glove
19 manufacturing line and equipment.

20 Example 1

21 A powder-free nitrile-coated natural rubber latex glove with an
22 intermediate natural rubber-nitrile layer between the glove and the nitrile coating

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1 was prepared as follows. Glove formers were pre-heated to about 60-70°C in an
2 oven for about 5 minutes. The preheated former then was dipped into a stirred,
3 water based coagulant dispersion maintained at a temperature between about
4 55°C to about 60°C. The coagulant-dipped former was then returned to the
5 heated oven for about 5 minutes to dry the coagulant layer.

6 The coagulant-coated former was dipped into a compounded natural
7 rubber latex for a time sufficient to produce the desired glove thickness. The
8 natural rubber latex was compounded with stabilizers, crosslinker, vulcanization
9 activator, vulcanization accelerators, antioxidant, antiozonant and white pigment.
10 The solid content of the compounded latex was about 38 wt. %. The former
11 bearing the coagulated latex was then removed from the compounded natural
12 rubber latex and immediately dipped into a second rubber blend latex for about
13 13 to about 15 seconds. The rubber blend latex comprised about 2.3%
14 compounded natural rubber latex and about 2.3% of carboxylated acrylonitrile
15 butadiene latex and about 95.4% water. The formulation of the compounded
16 natural rubber latex used in this rubber blend latex was the same as the one
17 used in the first latex dipping. The ratio of acrylonitrile/butadiene/carboxylic acid
18 for the nitrile rubber was 39/58/3.

19 The former was removed from the second rubber blend latex and dried in
20 a heated oven at about 58°C. The coagulated latex layer was leached in water
21 maintained at about 55°C to about 80°C for about 5 minutes. The former was
22 then dipped into a compounded nitrile blend latex with a total solid content of

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1 about 5% to form a coating on the intermediate natural rubber-nitrile blend layer.
2 The nitrile blend was comprised of a 50/50 blend of two carboxylated acrylonitrile
3 butadiene rubber latices with two different acrylonitrile/butadiene/carboxylic acid
4 ratios 39/58/3 and 39/55/6. The nitrile blend latex was further compounded with
5 1 part of sulfur dispersion (crosslinker), 1 part of ZDBC dispersion (vulcanization
6 accelerator), 3 parts of ZnO dispersion (vulcanization activator) and 15 parts of
7 silicone emulsion (SM 2140 obtained from General Electric). The dwell time for
8 the coating dipping was about 13 to about 15 seconds.

9 The cuff of the coated glove was beaded by a beader and the former was
10 placed in an oven maintained at about 110 - 136°C for about 20 minutes in order
11 to cure the glove. The former bearing the glove was then removed from the
12 oven and allowed to cool. The glove was then stripped from the former.

13 The glove was then post-processed by chlorination. First, the coated
14 glove was turned inside out manually and loaded into a chlorinator. The glove
15 was pre-rinsed 2 times for a total time of about 5 minutes. An aqueous chlorine
16 solution of about 300 ppm chlorine was added to the chlorinator and the gloves
17 tumbled for about 8.3 minutes. The chlorinated solution was then neutralized
18 with 50% sodium hydroxide solution for about 4 minutes. The glove was post-
19 rinsed 4 times for a total time of about 10 minutes. The glove was then
20 transferred to a tumbling washer for the lubrication process. Excess water was
21 removed from the glove by spinning the glove for about 2 minutes. The washer
22 was then filled with an aqueous lubrication solution comprised of about 0.5 wt %

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1 of cetylpyridinium chloride and 0.15 wt % of silicone emulsion. The glove was
2 tumbled in the lubrication solution for about 5 minutes. The lubrication solution
3 was drained and the glove was tumbled for an additional 5 minutes. The glove
4 was then removed from the tumbler washer and dried in a dryer with a heating
5 cycle of about 20 minutes at about 55°C and a cool down cycle for about 10
6 minutes. The glove was removed from the dryer and turned inside out manually.
7 The glove was dried again in the dryer at about 50°C for about 5 minutes and
8 allowed to cool down to room temperature for about 5 minutes.

9 The physical properties of the powder-free coated glove prepared as set
10 forth in Example 1 were measured according to ASTM D412-92. The gloves had
11 a tensile strength of 4323 psi, a tensile stress at 500% of 313 psi, and an
12 ultimate elongation of 1022%. The coefficient of friction (COF) of both the
13 outside and inside surfaces in the palm area of the glove were measured
14 according to ASTM D1894-95. The static and kinetic COF for the inside surface
15 were 0.72 and 0.46, respectively. The static and kinetic COF for the outside
16 surface were 1.22 and 1.61, respectively.

17 The donning characteristics of the glove were evaluated qualitatively with
18 respect to damp skin on a scale of 1 to 5, 1 being the worst with extreme
19 difficulties in donning the glove and 5 being the best with extreme ease in
20 donning the glove. This determination was made by having the glove donned by
21 a person with damp skin. The glove dons extremely well with respect to damp
22 and wet skin with a rating of 5.

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1 The adhesion of the coating was also evaluated qualitatively. In this test,
2 the coated glove surface was stretched to more than 500% and the coating was
3 rubbed repeatedly using the thumb. The coated surface was then visually
4 examined for coating flakes and powdery substance. The adhesion of the
5 coating was rated qualitatively on a scale of 1 to 5, 1 being the worst with the
6 entire coating flaking off the rubber substrate and 5 being the best with no visual
7 appearance of powdery substance on the surface of the glove. Using this test,
8 the adhesion of the inventive coating is quite good with a rating of 5 on a scale of
9 1 to 5, i.e., no flaking or shedding of the powder was observed after stretching
10 the glove to about 500% and rubbing it repeatedly with the thumb.

11 The finished glove was packaged as follows: a pair of gloves with a right
12 and a left hand was manually cuffed down to about 4 inches so that the inside
13 surface of the cuff was exposed to the outside. The left hand glove was laid flat
14 in the left side of the inner wrap paper with the thumb exposed outward and the
15 paper wrapped around the glove. The right hand glove was laid flat in the right
16 side of the inner wrap paper with the thumb exposed outward and the paper
17 wrapped around the glove. One wrapped glove was then flipped over the other
18 to produce a rectangular wallet-shaped packet. The inner wrap with a pair of
19 gloves was then placed in between a top web paper and a bottom web paper,
20 and thermally sealed on all sides 50 pairs of gloves were packed into a
21 dispenser box and 4 boxes were then packed into a carton. The packed gloves
22 were sterilized by gamma sterilization at a dose range of 28.1 KGy and 31.1
23 KGy.

1 The sterile glove had a tensile strength of 4309 psi, a tensile stress at
2 500% of 313 psi, and an ultimate elongation of 993%. The static and kinetic
3 COF for the inside surface were 0.37 and 0.15, respectively. The static and
4 kinetic COF for the outside surface were 0.6 and 0.8, respectively. The donning
5 characteristics of the sterile glove were excellent with a rating of 5 with respect to
6 damp skin on a scale of 1 to 5, i.e., no flaking or shedding of the powder was
7 observed after stretching the glove to about 500% and rubbing it repeatedly with
8 the thumb. The adhesion of the inventive coating was excellent with a rating of 5
9 on a scale of 1 to 5 (where about 4 to about 4.5 is the adhesion value exhibited
10 by commercially available glove coatings).

11 Example 2

12 A powder-free nitrile-coated natural rubber latex glove with an
13 intermediate natural rubber-nitrile layer between the glove and the nitrile coating
14 was prepared as set forth in Example 1 except that the chlorine concentration in
15 the aqueous chlorinated solution was adjusted to about 238 ppm and that the
16 lubricant solution was applied using a spraying process as follows.

17 After the chlorination process, the glove was transferred to an extractor
18 and excess water was removed from the glove by spinning the glove for about 5
19 minutes. The glove was then placed in a lubricator equipped with a spray gun.
20 The glove was tumbled in the dryer maintained at about 55°C for about 1 minute.
21 An aqueous lubrication solution comprised of about 0.5 wt % of cetylpyridinium
22 chloride and about 0.15 wt % of silicone emulsion was then sprayed on the glove

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1 while tumbling in the lubricator for about 156 seconds at 55°C. The spraying
2 was stopped for about 1 minute. The spraying process was repeated again two
3 more times. At the end of the third spraying, the glove was tumbled for about 25
4 minutes and allowed to cool for about 10 minutes. The glove was removed from
5 the lubricator and turned inside out manually. The glove was dried again in the
6 dryer at about 50°C for about 5 minutes and allowed to cool down to room
7 temperature for about 5 minutes.

8 The packed glove after gamma sterilization had a tensile strength of 4352
9 psi, a tensile stress at 500% of 341 psi, and an ultimate elongation of 984%.
10 The static and kinetic COF for the inside surface were 0.41 and 0.17,
11 respectively. The static and kinetic COF for the outside surface were 1.38 and
12 1.62, respectively. The donning characteristics of the sterile glove were
13 excellent with a rating of 5 with respect to damp skin on a scale of 1 to 5. The
14 adhesion of the coating was excellent with a rating of 5 on a scale of 1 to 5, i.e.,
15 no flaking or shedding of the powder was observed after stretching the glove to
16 about 500% and rubbing it repeatedly with the thumb (where about 4 to about
17 4.5 is the adhesion value exhibited by commercially available glove coatings).

18 Example 3

19 A powder-free coated natural rubber latex glove with an intermediate
20 natural rubber-nitrile layer between the glove and the nitrile coating was
21 prepared as set forth in Example 1 except that the chlorine concentration in the
22 aqueous chlorinated solution was adjusted to about 546 ppm.

Before sterilization, the glove had a tensile strength of 4324 psi, a tensile stress at 500% of 270 psi, and an ultimate elongation of 1032%. The static and kinetic COF for the inside surface were 0.39 and 0.28, respectively. The static and kinetic COF for the outside surface were 1.34 and 1.57, respectively. The donning characteristics of the sterile glove were excellent with a rating of 5 with respect to damp skin on a scale of 1 to 5. The adhesion of the coating was excellent with a rating of 5 on a scale of 1 to 5, i.e., no flaking or shedding of the powder was observed after stretching the glove to about 500% and rubbing it repeatedly with the thumb.

Example 4

A powder-free coated natural rubber latex glove with an intermediate natural rubber-nitrile layer between the glove and the nitrile coating was prepared as set forth in Example 1 except that the chlorine concentration in the aqueous chlorinated solution was adjusted to about 146 ppm.

Before sterilization, the glove had a tensile strength of 4310 psi, a tensile stress at 500% of 299 psi, and an ultimate elongation of 1042%. The static and kinetic COF for the inside surface were 1.06 and 0.64, respectively. The static and kinetic COF for the outside surface were 1.1 and 1.33, respectively. The donning characteristics of the sterile glove were good with a rating of 4 with respect to damp skin on a scale of 1 to 5. The adhesion of the coating was excellent with a rating of 5 on a scale of 1 to 5, i.e., no flaking or shedding of the

1 powder was observed after stretching the glove to about 500% and rubbing it
2 repeatedly with the thumb.

3 Examples 5-8

4 Powder-free coated natural rubber latex gloves with an intermediate
5 natural rubber-nitrile layer between the glove and the nitrile coating are prepared
6 as set forth in Examples 1, 2, 3 or 4 except that the total percent solid content for
7 the intermediate natural rubber-nitrile blend latex is adjusted to 1.5%, 2.0%,
8 2.5% and 10% [corresponding to Examples 5, 6, 7 and 8 respectively].

9 The gloves prepared as set forth in Examples 5-8 will have physical
10 properties similar to those described in Examples 1 through 4. The donning
11 characteristics of the gloves are excellent with a rating of 4 to 5 with respect to
12 damp skin on a scale of 1 to 5. The adhesion of the coatings are excellent with a
13 rating of 5 on a scale of 1 to 5.

14 Example 9

15 A powder-free nitrile-coated Neoprene glove with an intermediate natural
16 rubber-nitrile layer between the glove and the nitrile coating is prepared as
17 follows. A glove former is pre-heated to about 40°C to about 60°C in an oven.
18 The preheated former is dipped into a stirred, alcohol based coagulant
19 suspension maintained at less than about 55°C. The coagulant-dipped former is
20 then returned to the heated oven to dry the coagulant layer.

21 The coagulant-coated former is dipped into a compounded neoprene
22 copolymer latex which is maintained at about 20°C to about 28°C for a time

1 sufficient to produce the desired glove thickness. The neoprene copolymer latex
2 is compounded with stabilizers, crosslinker, vulcanization activator, vulcanization
3 accelerators, antioxidant, antiozonant and optionally, white or colored pigments.
4 The solid content of the compounded latex is about 48 wt. %. The former
5 bearing the coagulated latex is then removed from the compounded neoprene
6 copolymer latex and immediately dipped into a second rubber blend latex for a
7 time sufficient to produce the desired thickness. The rubber blend latex is
8 comprised of about 2.5% compounded natural rubber latex and about 2.5% of
9 carboxylated acrylonitrile butadiene latex and about 95% water. The formulation
10 of the compounded natural rubber latex used in this rubber latex is the same as
11 the one used in Example 1. The ratio of acrylonitrile/butadiene/carboxylic acid
12 for the nitrile rubber is 39/58/3.

13 The former is removed from the second rubber blend latex and leached in
14 water maintained at about 60°C. The former is then dipped into a compounded
15 nitrile blend latex with a total solid content of about 5% to form a coating on the
16 intermediate natural rubber-nitrile blend layer. The nitrile blend latex is
17 comprised of a 50/50 blend of two carboxylated acrylonitrile butadiene rubber
18 latices with two different acrylonitrile/butadiene/carboxylic acid ratios, 39/58/3
19 and 38/55/6. The formulation of the nitrile blend latex is the same as the one
20 used in Example 1.

21 The cuff of the coated glove is beaded and the former placed in an oven
22 maintained at about 150°C for about 20 minutes in order to cure the glove. The

1 former bearing the glove is then removed from the oven and allowed to cool.
2 The glove is stripped from the former. The glove is then post-processed by
3 chlorination/lubrication according to the process set forth in Example 1 except
4 that the chlorine concentration of the chlorinated solution is adjusted to about
5 344 ppm.

6 Before sterilization, the powder-free nitrile coated neoprene copolymer
7 glove prepared as set forth in Example 9 will have a thickness of about 7 to
8 about 9 mils in the palm area and a tensile strength of about 2700 to about 3200
9 psi, a tensile stress at 500% of about 220 to about 280 psi, and an elongation at
10 break of about 900 to about 1100%. The coated glove has excellent donning
11 characteristics with a rating of 5 with respect to damp skin on a scale of 1 to 5.
12 The adhesion of the coating is excellent with a rating of 5 on a scale of 1 to 5.

13 Example 10

14 A powder-free nitrile-coated neoprene copolymer glove with an
15 intermediate neoprene rubber-nitrile layer between the glove and the nitrile
16 coating is prepared as set forth in Example 9 with the exception that the second
17 rubber blend latex is comprised of about 2.5% compounded neoprene copolymer
18 latex and about 2.5% of carboxylated acrylonitrile butadiene latex and about
19 95% water. The formulation of the neoprene copolymer latex is the same used
20 in the first neoprene copolymer latex. The ratio of
21 acrylonitrile/butadiene/carboxylic acid for the nitrile rubber is 39/58/3.

Before sterilization, the powder-free nitrile coated neoprene copolymer glove before sterilization will have a thickness of about 0.007 to about 0.009 inches in the palm area and a tensile strength of about 2700 to about 3200 psi, a tensile stress at 500% of about 220 to about 280 psi, and an elongation at break of about 900 to about 1100%. The coated glove has excellent donning characteristics with a rating of 4 to 4.5 with respect to a damp skin on a scale of 1 to 5. The adhesion of the coating is excellent with a rating of 5 on a scale of 1 to 5.

Example 11

A powder-free nitrile-coated nitrile rubber glove with an intermediate natural rubber-nitrile layer between the glove and the nitrile coating is prepared as follows. A glove former is pre-heated to about 40°C to about 60°C in an oven. The preheated former then is dipped into a stirred, alcohol based coagulant suspension maintained at less than about 55°C. The coagulant layer which had been deposited on the glove former is then allowed to dry.

The coagulant-coated former is dipped into a compounded nitrile latex which is maintained at about 20°C to about 30°C for a time sufficient to produce the desired glove thickness. The nitrile latex is compounded with crosslinker, vulcanization activator, vulcanization accelerator, and optionally, antioxidant and white or colored pigment. The solid content of the compounded latex is about 30 wt. %. The former bearing the coagulated latex is then removed from the compounded nitrile latex and immediately dipped into a second rubber blend

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1 latex for a time sufficient to produce the desired thickness. The rubber blend
2 latex is comprised of about 2.5% compounded natural rubber latex and about
3 2.5% of carboxylated acrylonitrile butadiene latex and about 95% water. The
4 formulation of the compounded natural rubber latex used in this rubber blend
5 latex is the same as the one used in Example 1.

6 The former is removed from the second rubber blend latex and leached in
7 water maintained at about 25°C to about 45°C. The former is then dipped into a
8 compounded nitrile blend latex with a total solid content of about 5% to form a
9 coating on the intermediate natural rubber-nitrile blend layer. The nitrile blend
10 latex is comprised of a 50/50 blend of two carboxylated acrylonitrile butadiene
11 rubber lattices with two different acrylonitrile/butadiene/carboxylic acid ratios,
12 39/58/3 and 39/55/6. The formulation of the nitrile blend latex is the same as the
13 one used in Example 1.

14 The cuff of the coated glove is beaded and the former placed in an oven
15 maintained at about 125°C for about 20 minutes in order to cure the glove. The
16 former bearing the glove is then removed from the oven and allowed to cool.
17 The glove is stripped from the former. The glove is then post-processed by
18 chlorination/lubrication according to the process set forth in Example 1.

19 Before sterilization, the powder-free nitrile coated nitrile glove prepared as
20 set forth in Example 10 will have a thickness of about 0.004 to about 0.007
21 inches in the palm area and a tensile strength of about 2000 to about 5000 psi, a
22 tensile stress at 500% of about 600 to about 2000 psi, and an elongation at

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1 break of about 400% to about 900%. The coated glove has excellent donning
2 characteristics with a rating of 5 with respect to dry and damp skin on a scale of
10 3 1 to 5. The adhesion of the coating is excellent with a rating of 5 on a scale of 1
4 to 5. The adhesion of the coating is excellent with a rating of 5 on a scale of 1 to
15 5.

6 Example 12

20 7 A powder-free nitrile-coated nitrile glove with an intermediate rubber-nitrile
8 layer between the glove and the nitrile coating is prepared as set forth in
9 Example 11 with the exception that the second rubber blend latex is comprised
25 10 of about 2.5% compounded nitrile latex and about 2.5% of carboxylated
11 acrylonitrile butadiene latex and about 95% water. The formulation of the
30 12 compounded nitrile latex is the same used in the first compounded nitrile latex
13 that makes up the nitrile base glove. The ratio of
14 acrylonitrile/butadiene/carboxylic acid for the carboxylated nitrile rubber used in
35 15 the blend is 39/58/3.

16 Before sterilization, the powder-free nitrile coated nitrile glove will have a
40 17 thickness of about 0.004 to about 0.007 inches in the palm area, a tensile
18 strength of about 2000 to about 5000 psi, a tensile stress at 500% of about 600
19 to about 2000 psi, and an elongation at break of about 400% to about 900%.
45 20 The coated glove has excellent donning characteristics with a rating of 5 with
21 respect to dry and damp skin on a scale of 1 to 5. The adhesion of the coating is
50 22 excellent with a rating of 5 on a scale of 1 to 5.

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1 **Example 13**

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2 A powder-free nitrile-coated natural rubber latex glove with an
3 intermediate natural rubber-nitrile layer between the glove and the nitrile coating
4 was prepared as follows. Glove formers were pre-heated to about 60°-70°C in
5 an oven for about 5 minutes. The preheated former then was dipped into a
6 stirred, water based coagulant dispersion maintained at a temperature between
7 about 55°C to about 60°C. The coagulant-dipped former was then returned to
8 the heated oven for about 5 minutes to dry the coagulant layer.

9 The coagulant-coated former was dipped into a compounded natural
10 rubber latex for a time sufficient to produce the desired glove thickness. The
11 natural rubber latex was compounded with stabilizers, crosslinker, vulcanization
12 activator, vulcanization accelerators, antioxidant, antiozonant and white pigment.
13 The solid content of the compounded latex was about 36-37 wt. %. The former
14 bearing the coagulated latex was then removed from the compounded natural
15 rubber latex and immediately dipped into a second rubber blend latex for about
16 13 to 15 seconds. The rubber blend latex comprised about 8.0% compounded
17 natural rubber latex and about 2.5% of carboxylated acrylonitrile butadiene latex
18 and about 89.5% water. The formulation of the compounded natural rubber latex
19 used in this rubber blend latex was the same as the one used in the first latex
20 dipping. The ratio of acrylonitrile/butadiene/carboxylic acid for the nitrile rubber
21 was 39/58/3.

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1 The former was removed from the second rubber blend latex and dried in
2 a heated oven at about 140° – 145°C. The coagulated latex layer was leached
3 in water maintained at about 55°C to about 80°C for about 5 minutes. The
4 former was then dipped into a compounded nitrile blend latex with a total solid
5 content of about 4 – 5.5% to form a coating on the intermediate natural rubber-
6 nitrile blend layer. The nitrile blend was comprised of a 50/50 blend of two
7 carboxylated acrylonitrile butadiene latices with two different
8 acrylonitrile/butadiene/carboxylic acid ratios 39/58/3 and 39/55/6. The nitrile
9 blend latex was further compounded with 1 part of sulfur dispersion (crosslinker),
10 1 part of ZDBC dispersion (vulcanization accelerator), 3 parts of ZnO dispersion
11 (vulcanization activator) and 15 parts of silicone emulsion (SM 2140 obtained
12 from General Electric). The dwell time for the coating dipping was about 13 to
13 about 15 seconds.

14 The cuff of the coated glove was beaded by a beader and the former was
15 placed in an oven maintained at about 100 – 136 C for about 20 minutes in order
16 to cure the glove. The former bearing the glove was then removed from the
17 oven and allowed to cool. The glove was then stripped from the former.

18 The glove was then post-processed by chlorination. First, the coated
19 glove was turned inside out manually and loaded into a chlorinator. The glove
20 was pre-rinsed 2 times for a total time of about 5 minutes. An aqueous chlorine
21 solution of about 250 – 350 ppm chlorine was added to the chlorinator and the
22 gloves tumbled for about 8.3 minutes. The chlorinated solution was then

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1 neutralized with 50% sodium hydroxide solution for about 4 minutes. The glove
2 was post-rinsed 4 times for a total time of about 10 minutes. The glove was then
3 transferred to a tumbling washer for the lubrication process. Excess water was
4 removed from the glove by spinning the glove for about 2 minutes. The washer
5 was then filled with an aqueous lubrication solution comprised of about 0.8 wt %
6 of cetylpyridinium chloride and 0.1 wt % of silicone emulsion. The glove was
7 tumbled in the lubrication solution for about 5 minutes. The lubrication solution
8 was drained and the glove was tumbled for an additional 5 minutes. The glove
9 was then removed from the tumbler washer and dried in a dryer with a heating
10 cycle of about 20 minutes at about 55 C and a cool down cycle for about 10
11 minutes. The glove was removed from the dryer and turned inside out manually.
12 The glove was dried again in the dryer at about 50 C for about 5 minutes and
13 allowed to cool down to room temperature for about 5 minutes.

14 The powder-free coated gloves had a tensile strength of 3769 psi, a
15 tensile stress at 500% of 156 psi, and an ultimate elongation of 943%. The static
16 and kinetic COF for the inside surface were 0.44 and 0.32, respectively. The
17 static and kinetic COF for the outside surface were 1.90 and 2.98, respectively.
18 The glove dons extremely well with respect to damp and wet skin with a rating of
19 5. The adhesion of the inventive coating is excellent with a rating of 5 on a scale
20 of 1 to 5, i.e., no flaking or shedding of the powder was observed after stretching
21 the glove to about 500% and rubbing it repeatedly with the thumb.

22 The packed gloves were sterilized by electron beam sterilization at a dose

1 range of 29.4 KGy and 30.3 KGy. The sterile glove had a tensile strength of
2 4064 psi, a tensile stress at 500% of 288 psi, and an ultimate elongation of
3 908%. The donning characteristics of the sterile glove were excellent with a
4 rating of 5 with respect to damp skin on a scale of 1 to 5, i.e., no flaking or
5 shedding of the powder was observed after stretching the glove to about 500%
6 and rubbing it repeatedly with the thumb. The adhesion of the inventive coating
7 was excellent with a rating of 5 on a scale of 1 to 5.

Example 14

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9 A powder-free nitrile-coated rubber latex glove with an intermediate
10 natural rubber-nitrile layer between the glove and the nitrile coating was
11 prepared as set forth in Example 13 except that the nitrile blend latex was
12 compounded with 1 part of sulfur dispersion (crosslinker), 1 part of ZDBC
13 dispersion (vulcanization accelerator), 3 parts of ZnO dispersion (vulcanization
14 activator), 15 parts of silicone emulsion (SM 2140 obtained from General
15 Electric), and 1 part of an industrial biocide.

16 Before sterilization, the glove had a tensile strength of 3954 psi, a tensile
17 stress at 500% of 156 psi, and an ultimate elongation of 943%. The static and
18 kinetic COF for the inside surface were 0.43 and 0.29, respectively. The static
19 and kinetic COF for the outside surface were 1.72 and 2.75, respectively. The
20 donning characteristics of the sterile glove were excellent with a rating of 5 with
21 respect to damp skin on a scale of 1 to 5. The adhesion of the coating was
22 excellent with a rating of 5 on a scale of 1 to 5, i.e., no flaking or shedding of the

1 powder was observed after stretching the glove to about 500% and rubbing it
2 repeatedly with the thumb.

3 Example 15

4 A powder-free nitrile-coated natural rubber latex glove with an
5 intermediate natural rubber-nitrile layer between the glove and the nitrile coating
6 was prepared as set forth in Example 13 with the exception that the second
7 rubber blend latex is comprised of about 8.0% compounded natural rubber latex
8 and about 2.5% of acrylonitrile butadiene copolymer latex and about 89.5%
9 water.

10 Before sterilization, the powder-free nitrile coated natural rubber latex
11 glove will have a thickness of about 0.004 to about 0.0010 inches in the palm
12 area, a tensile strength of about 3500 to about 4800 psi, a tensile stress at 500%
13 of 150 to about 800 psi and an elongation at break of about 700 to about 1000%.
14 The coated glove has excellent donning characteristics with a rating of 5 with
15 respect to dry and damp kin on a scale of 1 to 5. The adhesion of the coating is
16 excellent with a rating of 5 on a scale of 1 to 5.

17 The foregoing description and examples relate only to preferred
18 embodiments of the present invention and numerous changes and modifications
19 may be made therein without departing from the spirit and scope of the invention
20 as defined in the following claims.

Claims

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2 What is claimed is:

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3 1. A powder-free elastomeric glove having an internal surface comprising a
4 first elastomeric layer, a second intermediate layer of a rubber blend
5 comprised of a natural rubber and a nitrile rubber disposed on said first
6 layer and a nitrile rubber coating disposed on said intermediate layer.

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7 2. The glove of claim 1 wherein the first elastomeric layer is comprised of
8 natural rubber.

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9 3. The glove of claim 1 wherein the first elastomeric layer is comprised of
10 neoprene rubber.

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11 4. The glove of claim 1 wherein the first elastomeric layer is comprised of
12 nitrile rubber.

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13 5. The glove of claim 1 wherein the first elastomeric layer is comprised of
14 synthetic polyisoprene rubber.

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15 6. The glove of claim 1 wherein the nitrile rubber coating is comprised of a
16 carboxylated acrylonitrile butadiene rubber.

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17 7. The glove of claim 1 wherein the nitrile rubber in the second intermediate
18 layer is comprised of a carboxylated acrylonitrile butadiene rubber having
19 an acrylonitrile content of about 25 to about 40 parts, a butadiene content
20 of about 55 to about 68 parts and a carboxylic acid content of about 3 to
50 21 about 6 parts.

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- 1 8. The glove of claim 6 wherein the nitrile rubber coating is comprised of a
2 blend of two carboxylated acrylonitrile butadiene rubbers with different
3 acrylonitrile/butadiene/carboxylic acid ratios.
- 4 9. The glove of claim 8 wherein each of the two carboxylated acrylonitrile
5 butadiene rubbers with different acrylonitrile/butadiene/carboxylic acid
6 ratios has an acrylonitrile content of about 25 to about 40 parts, a
7 butadiene content of about 55 to about 68 parts and a carboxylic acid
8 content of about 3 to about 6 parts.
- 9 10. A powder-free elastomeric glove having an internal surface comprising a
10 first elastomeric layer, a second intermediate layer of a rubber blend
11 comprised of a synthetic rubber and a nitrile rubber disposed on said first
12 layer and a nitrile rubber coating disposed on said intermediate layer.
- 13 11. The glove of claim 10 wherein the first elastomeric layer is comprised of
14 natural rubber.
- 15 12. The glove of claim 10 wherein the first elastomeric layer is comprised of
16 neoprene rubber.
- 17 13. The glove of claim 10 wherein the first elastomeric layer is comprised of
18 nitrile rubber.
- 19 14. The glove of claim 10 wherein the first elastomeric layer comprised of a
20 synthetic polyisoprene rubber.

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- 1 15. The glove of claim 10 wherein the first elastomeric layer is comprised of
2 the same synthetic rubber used in the intermediate layer.
- 3 16. The glove of claim 15 wherein the synthetic rubber is neoprene rubber.
- 4 17. The glove of claim 15 wherein the synthetic rubber is nitrile rubber.
- 5 18. The glove of claim 15 wherein the synthetic rubber is a synthetic
6 polyisoprene.
- 7 19. The glove of claim 10 wherein the nitrile rubber coating is comprised of a
8 carboxylated acrylonitrile butadiene rubber.
- 9 20. The glove of claim 19 wherein the nitrile rubber in the second intermediate
10 layer is comprised of a carboxylated acrylonitrile butadiene rubber having
11 an acrylonitrile content of about 25 to about 40 parts, a butadiene content
12 of about 55 to about 68 parts and a carboxylic acid content of about 3 to
13 about 6 parts.
- 14 21. The glove of claim 19 wherein the nitrile rubber coating is comprised of a
15 blend of two carboxylated acrylonitrile butadiene rubbers with different
16 acrylonitrile/butadiene/carboxylic acid ratios.
- 17 22. The glove of claim 21 wherein each of the two carboxylated acrylonitrile
18 butadiene rubbers with different acrylonitrile/butadiene/carboxylic acid
19 ratios has an acrylonitrile content of about 25 to about 40 parts, a
20 butadiene content of about 55 to about 68 parts and a carboxylic acid
21 content of about 3 to about 6 parts.

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- 1 23. A process for making a powder-free elastomeric glove having an internal
2 surface comprising a first elastomeric layer, a second intermediate layer of
3 a rubber blend comprised of a natural rubber and a nitrile rubber disposed
4 on said first layer and a nitrile rubber coating disposed on said
5 intermediate layer, comprising the steps of:
- 6 (a) dipping a former into a coagulant dispersion to deposit a
7 coagulant layer on the former;
- 8 (b) dipping the former with the deposited coagulant layer into an
9 elastomer to produce a second layer comprising coagulated
10 elastomer layer thereon;
- 11 (c) dipping the second layer of coagulated elastomer into a
12 blend of a natural rubber and a nitrile rubber dispersion to form an
13 intermediate layer on the glove;
- 14 (d) dipping the intermediate layer of a natural rubber and a
15 nitrile rubber into a powder-free dispersion comprised of a nitrile
16 rubber dispersion and a lubricant;
- 17 (e) curing the layers and the coating on the former;
- 18 (f) stripping the article from the former;
- 19 (g) turning the article so that the coated side of the article is on
20 the exterior of the article;
- 21 (h) treating the article to remove powder;
- 22 (i) drying the article;

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1 (j) turning the article so that the coated side of the article is on
2 the interior of the article; and

3 (k) drying the article.

4 24. The process of claim 23 wherein the step of treating the article to remove
5 powder comprises the step of immersing the article into an aqueous
6 chlorinated solution followed by the step of rinsing the article.

7 25. The process of claim 24 comprising the additional step of applying a
8 lubricant solution to the coated surface of the article after the chlorination
9 and rinsing steps.

10 26. The process of claim 23 comprising the additional step of leaching the
11 article in water after the former is dipped into the natural rubber and nitrile
12 rubber dispersion to produce the intermediate layer.

13 27. The process of claim 26 wherein the step of treating the article to remove
14 powder comprises the step of immersing the article into an aqueous
15 chlorinated solution followed by the step of rinsing the article.

16 28. The process of claim 27 comprising the additional step of applying a
17 lubricant solution to the coated surface of the article after the chlorination
18 and rinsing steps.

19 29. A process for making a powder-free elastomeric glove having an internal
20 surface comprising a first elastomeric layer, a second intermediate layer of
21 a rubber blend comprised of a synthetic rubber and a nitrile rubber

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- 1 disposed on said first layer and a nitrile rubber coating disposed on said
2 intermediate layer, comprising the steps of:
- 3 (a) dipping a former into a coagulant dispersion to deposit a
4 coagulant layer on the former;
- 5 (b) dipping the former with the deposited coagulant layer into an
6 elastomer to produce a second layer comprising coagulated elastomer
7 layer thereon;
- 8 (c) dipping the second layer of coagulated elastomer into a blend of
9 a synthetic rubber and a nitrile rubber dispersion to form an
10 intermediate layer on the glove;
- 11 (d) dipping the intermediate layer of a synthetic rubber and a nitrile
12 rubber into a powder-free dispersion comprised of a nitrile rubber
13 dispersion and a lubricant;
- 14 (e) curing the layers and the coating on the former;
- 15 (f) stripping the article from the former;
- 16 (g) turning the article so that the coated side of the article is on the
17 exterior of the article;
- 18 (h) treating the article to remove powder;
- 19 (i) drying the article;
- 20 (j) turning the article so that the coated side of the article is on the
21 interior of the article; and

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1 (k) drying the article.

2 30. The process of claim 29 wherein the step of treating the article to remove
3 powder comprises the step of immersing the article into an aqueous
4 chlorinated solution followed by the step of rinsing the article.

5 31. The process of claim 30 comprising the additional step of applying a
6 lubricant solution to the coated surface of the article after the chlorination
7 and rinsing steps.

8 32. The process of claim 29 comprising the additional step of leaching the
9 article in water after the former is dipped into the synthetic rubber and
10 nitrile rubber dispersion to produce the intermediate layer.

11 33. The process of claim 32 wherein the step of treating the article to remove
12 powder comprises the step of immersing the article into an aqueous
13 chlorinated solution followed by the step of rinsing the article.

14 34. The process of claim 33 comprising the additional step of applying a
15 lubricant solution to the coated surface of the article after the chlorination
16 and rinsing steps.

17 35. A powder-free elastomeric glove having an internal surface comprising a
18 first elastomeric layer and a second intermediate layer of a rubber blend
19 comprised of a natural rubber and a nitrile rubber disposed on said first
20 layer.

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- 1 36. A powder-free elastomeric glove having an internal surface comprising a
2 first elastomeric layer and a second intermediate layer of a rubber blend
3 comprised of a synthetic rubber and a nitrile rubber disposed on said first
4 layer.
- 5 37. A process for making a powder-free elastomeric glove having an internal
6 surface comprising a first elastomeric layer, a second intermediate layer of
7 a rubber blend comprised of a natural rubber and a nitrile rubber disposed
8 on said first layer and a nitrile rubber coating disposed on said
9 intermediate layer comprising the steps of;
- 10 (a) dipping a former into a coagulant dispersion to deposit a
11 coagulant layer on the former;
- 12 (b) dipping the former with the deposited coagulant layer into an
13 elastomer to produce a second layer comprising coagulated
14 elastomer layer thereon;
- 15 (c) dipping the second layer of coagulated elastomer into a
16 blend of natural rubber and a nitrile rubber dispersion to form an
17 intermediate layer on the glove;
- 18 (d) leaching the former with the coagulated elastomer layer and
19 the intermediate rubber blend layer in water;
- 20 (e) dipping the intermediate layer of a natural rubber and a
21 nitrile rubber into a powder-free dispersion comprised of a nitrile
22 rubber dispersion and a lubricant;

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- 1 (f) curing the layers and the coating on the former;
- 2 (g) stripping the article from the former;
- 3 (h) treating the article to remove powder by immersing the
- 4 article into an aqueous chlorinated solution;
- 5 (i) rinsing the article; and
- 6 (j) drying the article.
- 7 38. A process for making a powder-free elastomeric glove having an internal
- 8 surface comprising a first elastomeric layer, a second intermediate layer of
- 9 a rubber blend comprised of a synthetic rubber and a nitrile rubber
- 10 disposed on said first layer and a nitrile rubber coating disposed on said
- 11 intermediate layer comprising the steps of:
- 12 (a) dipping a former into a coagulant dispersion to deposit a
- 13 coagulant layer on the former.
- 14 (b) dipping the former with the deposited coagulant layer into an
- 15 elastomer to produce a second layer comprising coagulated
- 16 elastomer layer thereon;
- 17 (c) dipping the second layer of coagulated elastomer into a
- 18 blend of synthetic rubber and a nitrile rubber dispersion to
- 19 form an intermediate layer on the glove;
- 20 (d) leaching the former with the coagulated elastomer layer and
- 21 the intermediate rubber blend layer in water;

- 5
- 1 (e) dipping the intermediate layer of a synthetic rubber and a
- 2 nitrile rubber into a powder-free dispersion comprised of a
- 10 3 nitrile rubber dispersion and a lubricant;
- 4 (f) curing the layers and the coating on the former;
- 15 5 (g) stripping the article from the former;
- 6 (h) treating the article to remove powder by immersing the
- 20 7 article into an aqueous chlorinated solution;
- 8 (i) rinsing the article; and
- 25 9 (j) drying the article.

10 39. The glove of claim 1 wherein the nitrile rubber coating is comprised of an

11 acrylonitrile butadiene rubber.

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12 40. The glove of claim 1 wherein the nitrile rubber in the second intermediate

13 layer is comprised of an acrylonitrile butadiene rubber having an

35 14 acrylonitrile content of about 25 to about 40 parts and a butadiene content

15 of about 50 to about 75 parts.

40 16 41. The glove of claim 1 wherein the total solid content of the dispersion from

17 which the intermediate rubber blend layer is formed is less than about

18 45%.

45 19 42. The glove of claim 1 wherein the nitrile rubber coating is comprised of a

20 blend of nitrile rubber and synthetic rubber.

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- 1 43. A powder-free elastomeric article having an internal surface comprising a
2 first elastomeric layer, a second intermediate layer of a rubber blend
3 comprised of a natural rubber and a nitrile rubber disposed on said first
4 layer and a nitrile rubber coating disposed on said intermediate layer.
- 5 44. The article of claim 43 wherein the first elastomeric layer is comprised of
6 natural rubber.
- 7 45. The article of claim 43 wherein the first elastomeric layer is comprised of
8 neoprene rubber.
- 9 46. The article of claim 43 wherein the first elastomeric layer is comprised of
10 nitrile rubber.
- 11 47. The article of claim 43 wherein the first elastomeric layer is comprised of
12 synthetic polyisoprene rubber.
- 13 48. The article of claim 43 wherein the nitrile rubber coating is comprised of a
14 carboxylated acrylonitrile butadiene rubber.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03135

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A41D 19/015; B32B 25/14; C08L 33/02, 20.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 2/161.6, 161.7, 167, 168; 428/35.7, 36.8, 36.91, 447, 492, 495, 515, 519, 520, 521, 522.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST (Derwent and USPAT), search terms: acrylonitrile, butadiene, carboxyl, carboxylated, glove.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,069,965 A (ESEMPLARE) 03 December 1991, col. 2, lines 30+, col. 5, line 15-16, line 27, col. 7 line 9 through col. 8, line 37.	1-48
Y	US 5,084,514 A (SZCZETCHURA et al) 28 January 1992, col. 1, lines 17+, col. 3, lines 19+ and 50+, col. 5, lines 32=35.	1-48
Y	US 5,742,943 A (CHEN) 28 April 1998, abstract.	3, 4, 12, 13, and 45-48
Y, P	US 5,910,533 A (GHOSAL et al) 08 June 1999, col. 1, line 12, col. 6, lines 35-60.	15-18 and 23-48

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 APRIL 2000

Date of mailing of the international search report

02 MAY 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

SANDRA NOLAN

Telephone No. (703) 308-2331

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03135

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03135

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

2/161.6, 161.7, 167, 168; 428/35.7, 36.8, 36.91, 447, 492, 493, 515, 519, 520, 521, 522.